REPORT DOCUMENTATION PAGE

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12-10-2011	Final Report	1-Oct-2008 - 31-Dec-2009

4. TITLE AND SUBTITLE	
Bio-Inspired Dynamically Tunable Polymer-Based Filters for Multi-Spectral Infrared Imaging	5a. CONTRACT NUMBER W911NF-08-1-0494
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 8G10AR
6. AUTHORS Daniel E. Morse	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
University of California - Santa Barbara Office of Research The Regents of the University of California Santa Barbara, CA 93106 -2050	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 55322-PH-DRP.2

12. DISTRIBUTION AVAILABILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

The objective of this collaborative research undertaken by UCSB and Raytheon Vision Systems, Inc. was to translate the unique, enabling principles recently learned from UCSB’s analyses of the molecular mechanisms driving dynamically tunable reflectance in cephalopod skin to the development of a high-gain, dynamically tunable, polymer-based IR filter. Based on a revolutionary but simple new "bio-inspired" design, our prototype devices are lightweight and silent; they require low power and are manufacturable at low-cost. The filters we are developing

15. SUBJECT TERMS

Filters, Multi-Spectral, IR, polymer, tunable, cephalopod

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Daniel Morse
UU	UU	UU	UU		19b. TELEPHONE NUMBER 805-893-3157

Report Title

Bio-Inspired Dynamically Tunable Polymer-Based Filters for Multi-Spectral Infrared Imaging

ABSTRACT

The objective of this collaborative research undertaken by UCSB and Raytheon Vision Systems, Inc. was to translate the unique, enabling principles recently learned from UCSB's analyses of the molecular mechanisms driving dynamically tunable reflectance in cephalopod skin to the development of a high-gain, dynamically tunable, polymer-based IR filter. Based on a revolutionary but simple new "bio-inspired" design, our prototype devices are lightweight and silent; they require low power and are manufacturable at low-cost. The filters we are developing are comprised of two lightweight polymers in a nanostructured film that synergistically interact in response to an applied electric field to change both their refractive index and thickness, thus providing an exponential change in wavelength transmission in response to small changes in voltage. In contrast, present mechanical systems for tuning in the IR are heavy, slow, power-hungry and costly. Even tnext generation MEMS-driven Fabry-Perot filters are mechanically vulnerable, expensive and bulky in comparison to the thin-film polymer system we are developing for direct deposition on the focal plane array. Results of this first year's seedling effort, culminating in an electrically switchable, lightweight polymer-based shutter and aperture for IR detectors, are described in our publication (Holt et al., 2010).

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
2011/10/10 1!	1	Amanda L. Holt, Justin G.A. Wehner, Andreas Hammp, Daniel E. Morse. Plastic Transmissive Infrared Electrochromic Devices, Macromolecular Chemistry and Physics, (07 2010): 0. doi: 10.1002/macp.201000096

TOTAL: 1

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

06/08 Invited Lecture, “Bio-Inspired Nanofabrication of Semiconductors and Dynamically Adaptive Optical Materials” 3rd International Conference “Smart Materials, Structures and Systems”, Acireale, Catania Italy

08/08 Invited Lecture, “Dynamically Adaptive Biophotonics: Protein Phosphorylation Drives Changes in Iridescence in Squid” American Chemical Society Symposium, Philadelphia, PA

11/08 Invited Lecture, “Dynamically Adaptive Biophotonics: Protein Phosphorylation Drives Changes in Iridescence in Squid Inspiring New Approaches to Dynamically Tunable Optical Materials” BioNano Workshop, Kawagoe, Japan

11/08 Invited Lecture, “New Pathway for Encoding Self-Assembly and Emergent Properties” Molecular Foundry User Meeting 2008, Berkeley, CA

12/08 Invited Lecture, “Dynamically Adaptive Biophotonics: Protein Phosphorylation Drives Changes in Iridescence in Squid, Inspiring New Approaches to Dynamically Tunable Optical Materials” 3rd BioNano Workshop, Kawagoe, Japan

01/09 Invited Talk, “New Pathways for Encoding Self-Assembly and Emergent Properties”, Daniel E. Morse, Igor Mezic, Meredith Murr, Gunjan Thakur Society for Biological Engineering 2nd International Conference on Biomolecular Engineering, Santa Barbara, CA

02/09 Invited Lecture, “Dynamically Adaptive Biophotonics: Protein Phosphorylation Drives Changes in Iridescence in Squid, Inspiring New Approaches to Dynamically Tunable Optical Materials; and New Pathways for Encoding Self-Assembly and Emergent Properties” Knight Lecture University of Akron, Akron OH (Advanced Lecture)

04/09 Invited Speaker, “Dynamically Tunable Biophotonics: Camouflage and Communication in Squid Inspire New Approaches to Tunable Optical Materials" MCDB Seminar, UCSB

10/09 Invited Plenary Lecture, “Nanotechnology in Nature” INSPIRE BioNano International Conference, Dublin, Ireland

10/09 Invited Lecture, “Biological Systems Inspire New Pathways to High-Performance Materials for Energy and Photonics” Bioengineering Insights 2009, UCSB

Number of Presentations: 10.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Daniel DeMartini	0.36	
FTE Equivalent:	**0.36**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Amanda Holt	0.40
Zhongtao Li	0.11
Fang Qian	0.17
FTE Equivalent:	**0.68**
Total Number:	**3**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Yegermal Asnake	0.01	Molecular Biology
Meredith Lujan	0.07	
FTE Equivalent:	**0.08**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Brigit Schwenzer	0.08
FTE Equivalent:	**0.08**
Total Number:	**1**

Sub Contractors (DD882)

1 a. Raytheon Vision Systems

1 b. Raytheon Vision Systems
75 Coromar Drive B2/8
Goleta CA 93117

Sub Contractor Numbers (c): W911NF-08-1-0494

Patent Clause Number (d-1): None

Patent Date (d-2):

Work Description (e): RVS shall deliver reports to UCSB on:

Sub Contract Award Date (f-1): 10/1/2008 12:00:00AM

Sub Contract Est Completion Date(f-2): 12/31/2009 12:00:00AM

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75 Coromar Drive B2/8
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Sub Contractor Numbers (c): W911NF-08-1-0494

Patent Clause Number (d-1): None

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Sub Contract Award Date (f-1): 10/1/2008 12:00:00AM

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Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Date: May 1, 2010

RE: **FINAL REPORT:**
Contract # 55322-PH-DRP
Bio-Inspired Dynamically Tunable Polymer-Based Filters for Multi-Spectral Infrared Imaging

- Number of Ph.D., M.S., and B.S. degrees awarded to students supported by the grant:
2 B.S awarded; 1 Ph.D. in progress.

- Publication:

Holt, A.L., J. G. A. Wehner, A. Hammp and D. E. Morse. 2010. Plastic transmissive infrared electrochromic devices. Macromolecular Chemistry & Physics. 211: 1701-1707. DOI: 10.1002/macp.201000096.

- Presentations:

D.E. Morse:

06/08	Invited Lecture, "Bio-Inspired Nanofabrication of Semiconductors and Dynamically Adaptive Optical Materials"	3rd International Conference "Smart Materials, Structures and Systems", Acireale, Catania Italy
08/08	Invited Lecture, "Dynamically Adaptive Biophotonics: Protein Phosphorylation Drives Changes in Iridescence in Squid"	American Chemical Society Symposium, Philadelphia, PA
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12/08	Invited Lecture, "Dynamically Adaptive Biophotonics: Protein Phosphorylation Drives Changes in Iridescence in Squid, Inspiring New Approaches to Dynamically Tunable Optical Materials"	3rd BioNano Workshop, Kawagoe, Japan
01/09	Invited Talk, "New Pathways for Encoding Self-Assembly and Emergent Properties", Daniel E. Morse, Igor Mezic, Meredith Murr, Gunjan Thakur	Society for Biological Engineering 2nd International Conference on Biomolecular Engineering, Santa Barbara, CA

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04/09	Invited Speaker, “Dynamically Tunable Biophotonics: Camouflage and Communication in Squid Inspire New Approaches to Tunable Optical Materials"	MCDB Seminar, UCSB
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10/09	Invited Lecture, “Biological Systems Inspire New Pathways to High-Performance Materials for Energy and Photonics”	Bioengineering Insights 2009, UCSB

Supervised by D. Morse:

08/08	Invited Talk, “Plasmonic Lattices”, Andrea Tao	Gordon Research Conference on Plasmonics, Tilton, NH
04/09	Invited Talk, “Self-Assembled Plasmonic Crystals”, Andrea R. Tao, Daniel P. Ceperley, Andrew M. Neureuther, Peidon Yang, presented by Andrea R. Tao	6th Annual Foundations of Nanoscience Conference on Self-Assembled Architecture and Devices, Snowbird, UT
05/09	Invited Talk, “Biological Inspiration for Dynamically Adaptive Camouflage”, Alison Sweeney, Daniel DeMartini, Michi Izumi, Amanda Holt, and Daniel E. Morse, presented by Alison Sweeney	Reliance 21 Materials & Processes, Research and Engineering, Technology Focus Team, Annual Planning Workshop, St. Michaels, MD
10/09	Invited Poster, “ Changes in Reflectin Phosphorylation Drives Iridescence in Squid”, Daniel DeMartini, Michi Izumi, Andrea Tao and Dan Morse, presented by Daniel DeMartini	BioEngineering Insights Conference, Santa Barbara, CA

TECHNICAL REPORT:

In our recently completed Seedling project, DARPA Seedling 55322-PH-DRP, "Bio-Inspired Dynamically Tunable Polymer-Based Filters for Multispectral IR," we investigated aspects of electrochromics, electrostrictives, and bulk heterostructures. In our recent publication (Holt et. al., 2010) we describe our progress regarding higher-level device design metrics and measurements, materials characterization, and work products related to our efforts. We summarize our objectives, potential benefit to the Army, collaboration and accomplishments below:

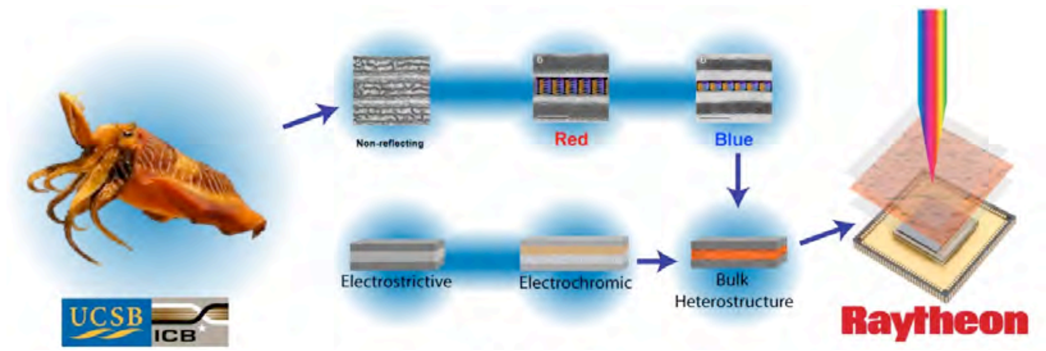

Figure 1. Schematic illustrating the proposed translation of recently discovered biophotonic mechanisms to enable development of a novel polymer-based, electrically tunable filter for multispectral IR detection.

Objective:

Our objective was to translate the unique, enabling principles recently learned from UCSB's analyses of the molecular mechanisms driving the dynamically tunable reflectance in cephalopod skin to the development of a *high-gain, dynamically tunable, polymer-based IR filter*.

Unique Advantages for Military and Civilian Applications:

Based on a revolutionary but simple new "bio-inspired" design, we proposed to make these dynamically tunable IR filters uniquely high-gain, lightweight, low power and low-cost. The filters we are developing are comprised of two lightweight polymers in a nanostructured film that synergistically interact with one another in response to an applied electric field to modify both their refractive index and thickness, thus providing an exponential change in wavelength transmission in response to small changes in applied voltage. In contrast, present systems for tuning in the IR are heavy, slow, mechanical and costly to manufacture; they also consume high power loads. Even the next generation of MEMS-driven Fabry-Perot filters is mechanically vulnerable, expensive and bulky in comparison to the thin-film polymer system we envision depositing directly on the focal plane array. Pixelation (the next step beyond the first proof-of-principle proposed here) will provide multidimensional imaging capability.

In addition to the numerous military applications of the new capability we proposed, firefighters, rescue workers, urban and agricultural planners, land-use and water resource managers and medical diagnosticians all will benefit from the proposed advance in multispectral infrared imaging capability.

Close Collaboration Between UCSB and Raytheon Using Innovative Bio-Inspired Approach:

Our closely collaborative team of UCSB and Raytheon researchers has been working together for the past two years to translate the unique enabling principles recently learned from UCSB's discoveries of the molecular mechanisms driving the dynamically tunable reflectance in cephalopod skin to the development of an electrically tunable, polymer-based infrared multispectral filter as illustrated schematically in figure 1, above. We propose here an innovative approach to combine elements of electrostrictive and electrochromic materials to form a bulk heterostructure device.

The overall technical approach is to build a lightweight, tunable filter beginning with a single organic polymeric layer that can change thickness and a single layer that can change refractive index. By combining these layers into one device that is capable of changing both thickness and refractive index (as the protein-based intracellular Bragg reflectors in cephalopods do), a multi-layer device can be constructed to tune reflection/transmission across the near infrared (NIR). The synergistic effects of electrostriction and electrochromicity are proposed to provide a high-gain tuning of wavelength with low power consumption. **This approach is "biologically inspired," as it is derived from our discovery that the dynamically tunable biophotonic structural colors in the squid skin are produced by the synergistic and simultaneous interaction of changes in the refractive index, thickness and spacing of protein-based Bragg reflectors in the squid skin (cf. our publications: Izumi et al., 2010; Tao et al., 2010, refs. 1 & 2). We therefore are aiming at a "translation" of this lesson based on the synergistic interaction of polymer thin-films that will produce both changes in refractive index and thickness to yield a synergistically high-gain tunable optical response to low-voltage electrical activation.**

Electrochromics:

Early in the project, it became clear that when conjugated polymer electrochromics were subjected to bias, the change in the imaginary part of their refractive index overshadowed the change in the real part leading to high optical absorption. This finding indicated that the current electrochromic materials were not suitable for a tunable filter but rather a shutter. Due to this intriguing find, the project's focus shifted towards improving the shutter device. This exercise served as an important stepping-stone in moving towards a tunable spectral filter by demonstrating that, in order to achieve success with electrochromics, a new generation of conjugated polymers was needed.

Higher-Level Device Design (Electrochromic-Based IR Shutter):

The first initiative in the device design work consisted of determining a standard device structure, consisting of the following layers of material (Holt et al., 2010): Substrate/ITO/P3HT/Electrolyte/ITO/Substrate. Once this "standard" structure was fully characterized, the work shifted to modifying the structural layers and materials in order to improve device performance. The standard structure exhibited good near IR (NIR) transmission (>95%) in the off state, while suppressing transmission to 5-10% in the on state. The on/off switch time of the standards structure, however, was initially very slow, 45s on and 160 s off. Through structural and material modifications, we were able to significantly improve switch speed and decrease transition period, down to 0.4 s on and 0.8 s off.

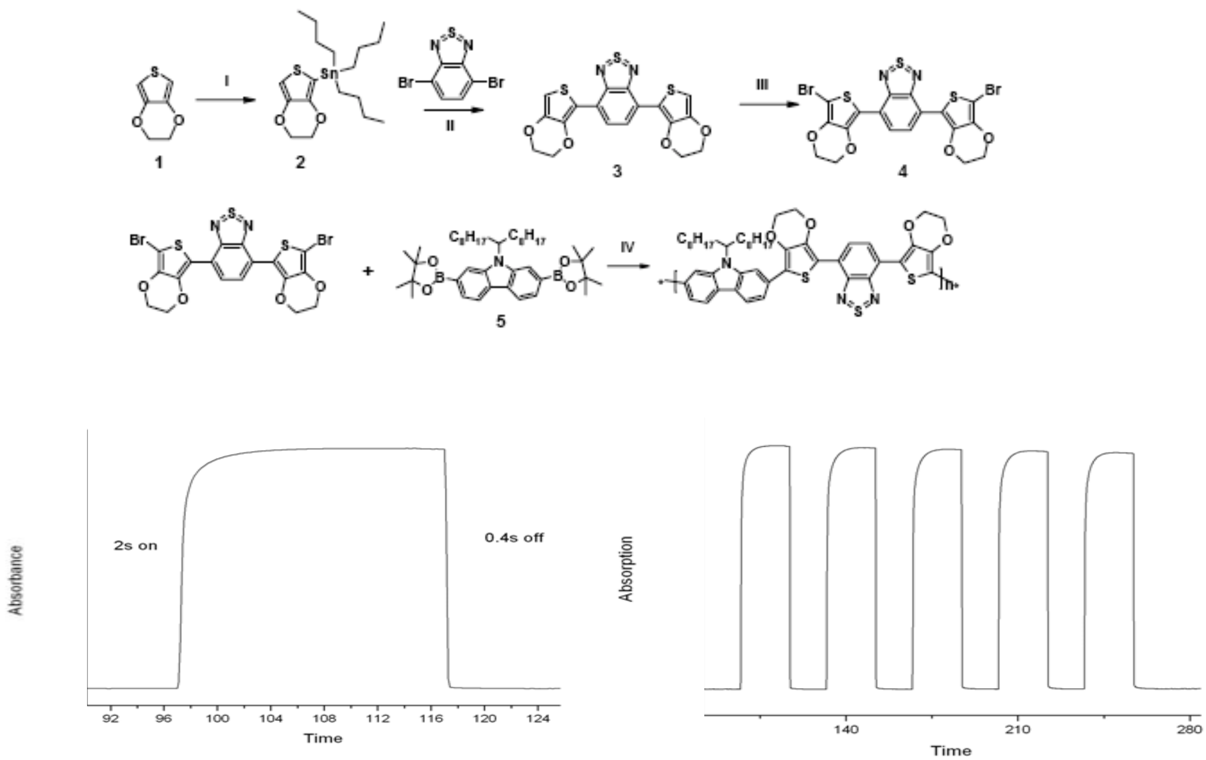

Figure 4. (Top) Synthesis of novel electrochromic polymers giving improved optical contrast and faster switching speeds for electrically switchable polymer-based shutter for IR detectors. (Bottom) Electrochromic shutter performance in the NIR.

Electrostrictives:

To further improve device performance, we began investigating polymeric materials that are able to change physical thickness for use in filtering applications. Two primary types of electroactive polymers (EAPs) were investigated: 1) field-activated EAPs and 2) ionic EAPs. Examples of field activated EAPs include: dielectric elastomers, ferroelectric polymers (i.e. PVDF), electrostrictive graft elastomers, and liquid crystal elastomers. Examples of Ionic EAPs include: ionic polymer gels, ionomeric polymer-metal composites (IPMCs), conducting polymers, and single and multi-wall carbon nanotubes. During the Seedling execution we conducted an extensive literature review, ordered and began characterizing some of the materials. Using a modified Conductance-AFM, we measured the optimum change in thickness of the best electrostrictive polymer found thus far to be 300% at 12 volts activation..

Combining Electrochromics and Electrostrictives:

Inspired by our recent discoveries of the mechanism underlying the dynamically tunable biophotonic system in the squid, in which we discovered that the observed high gain color change is driven by the synergistic interaction of a simultaneous change in refractive index, thickness and spacing of the responsible Bragg reflectors, we are seeking a similar advantage in the synthetic system. A number of methods for achieving a material that changes both refractive index and thickness were investigated, including bulk heterostructure polymers and multi-region polymers constructed by dip-coating polystyrene balls or infilling defined regions with balls-in-

solution and allowing solution to drain via specially constructed photo-resist channels. Efforts for combining electrostrictive and electrochromic materials showed promising progress, but without further material development of the electrostrictive materials themselves, this effort cannot achieve its target metrics. Additional support from DARPA is being sought at this time to enable the necessary further investigations.